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Progress Report

Publications:

a) Utilization of a System Employing the Selective Permeation of Helium through a Unique Membrane of Teflon as an Interface for Gas Chromatograph and Mass Spectrometer
Lipsky, S.R., Horvath, C.G., and McMurray, W.J. Anal. Chem. 38, 1585, 1966.

b) The Analysis of Complex Organic Compounds by Fast Electrical Scanning High Resolution Mass Spectrometry and Gas Chromatography
Lipsky, S.R., McMurray, W.J., and Horvath, C.G. Proceedings of the Sixth International Symposium on Gas Chromatography and Associated Techniques, Editor A.B. Littlewood, The Institute of Petroleum, February 1967 (reprints will be available by March).

Direct Digitization of Fast Scan High Resolution Mass Spectra

After approximately a year of development work, we are delighted to report that for the first time, high resolution mass spectra (M/ΔM 1:10,000 plus) have been obtained by direct digitization of the output of the mass spectrometer. The digitized mass spectrum is stored directly on digital magnetic tape. From a second pass of the tape, the peak profiles are extracted, the centers of the peak determined and with the aid of a calibration compound, the times are converted into accurate masses and then into elemental compositions. In contrast to our previous fast scanning high resolution system whereby data was initially obtained by recording on high quality analog FM tape and then playing back at a slower speed via a galvanometer recorder prior to digitization (by means of an analog to digital converter), the direct digitization technique permits us to utilize the full dynamic ratio (signal to noise) that is inherent in mass spectrometer on a single channel. Several other outstanding advantages were achieved by the development of this method. One is now able to obtain better accuracy in the determination of isotope ratios within the limits of statistics. The direct digitization method also appears to be a much more convenient method of operation. The prior use in this laboratory of FM analog tape as an intermediate recording technique while being a generally satisfactory method of operation, requires several channels of recording to approach the dynamic range obtained from the direct method. On several occasions it also gave rise to 'tape failure'. This is now easily avoided with the new system. Moreover the direct digitization method requires less time in processing data

than the multichannel analog method. Finally, and most important, the accuracy of mass measurement by both methods is on the average better than ten parts per million. However it appears at this time, that the standard deviations in the mass measurements is less for the direct digitization technique than for analog tape systems employing a single channel of log attenuated information.

To provide the ultimate in versatility, flexibility and reliability the system is now so arranged whereby as a back up analog recordings of the mass spectra are made simultaneously with direct digitization.

The results of this effort are now being compiled and will be submitted for publication within the next 1-2 months.

Enrichment Devices:

Further efforts have been expended in this laboratory to continuously improve the efficiency and reliability of enrichment devices which are used to interface the gas chromatograph with the mass spectrometer. In a prior report, we described a totally new concept for removing the carrier gas (either helium or hydrogen) prior to entry of the chromatographic effluent into the ion source of the mass spectrometer. This concept utilized a thin teflon capillary tube which permitted the preferential diffusion of helium (with some loss of solute) out of the system. Variables determining the rate of diffusion of helium as well as solute were described at that time. After optimizing the operating parameters (temperature, partial pressures across the membrane, surface area, flow characteristics, etc., thru the tube) it was theorized that additional efficiency made be readily procured by decreasing the thickness of the teflon membrane. In practice we found that this was a difficult goal to achieve if one adhered to a tubular (capillary) configuration. Apparently our present tubes (0.020" o.d. x 0.010" i.d. with a 0.005" wall) are the thinnest systems that can be fabricated conveniently. Since teflon in sheet form can be obtained in a wide variety of thicknesses extending down by at least an order of magnitude (over that obtained in tubular form) a single and double stage system is now being designed to take advantage of the availability of these materials. The effects of altering the aforementioned parameters on the overall efficiency of the system will be determined within the next few months.

Pyrolysis Studies:

From work conducted in our laboratories as well as others throughout the world it has been found that combined pyrolysis - gas chromatography-mass spectrometry techniques can be exceedingly valuable in obtaining information in the form of a 'fingerprint' fragmentation pattern which can be helpful in elucidating the structure of non-volatile compounds. However, upon careful examination of the various parameters involved in the combined method, it soon became known that slight alterations here gave rise to different pyrolysis profiles which accordingly were difficult to reproduce from laboratory to laboratory. These difficulties involved:

a) pyrolysis temperature and the time required to reach this temperature

b) the nature of the carrier gas
   1. the flow rate of the carrier gas

c) how pyrolysis was conducted i.e. by means of ceramic boats or metallic filaments. Results here depended upon the mass of the boat or the history (age, degree of cleanliness etc.) of the filament and the time required to reach temperature

d) sample size. The larger the sample, the greater the number of rearrangements occurring which in turn usually gave rise to a larger number of pyrolysis products, some of which were difficult to interpret in the light of the chemical structure of the original starting material

e) the design of the pyrolyzer.
   1. Condensation of volatile products on the walls of the pyrolyzer was to be avoided
   2. The 'dead' zone between the pyrolyzer and the chromatographic column has to be minimized in order to reduce the turbulence and enhanced gaseous diffusion of the volatile products which would give rise to poor resolution of the eluted peaks.

Because of these observations it is apparent that new design concepts for a pyrolysis system have to be developed for a prototype laboratory version of a miniature preflight gas chromatograph-mass spectrometer instrument. Other techniques for rapid pin point heating by means of radio frequency or laser systems will have to be explored. We expect to have a new pyrolysis system ready for testing within the next 3 to 4 months. Practical tests will

then be carried out on 10-20 milligram quantities of some 20 different types of 'soil' samples. Known quantities of a different array of pure organic compounds will be added to different 'sterile' soil carriers and analyzed by this system.

It is hoped that a simple, reliable and reproducible system can be obtained which will allow one to determine the presence of pyrolysis products that are easily identifiable by means of the gas chromatography mass spectrometry system now being designed for the Voyager landing mission in the 1970's.